PRIMARY HYDROGEN-OXYGEN FUEL CELLS FOR SPACE

By

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Summary

By 1975, Grove-type fuel cells may reach 70% gross thermal efficiency, with 3-5% for parasitic power. Cell-degradation rates should be 4 microvolts/hr or less, and system specific weight 60-80 lbs/kw of average load, with maintenance-free life up to 1 year. A better cathodic catalyst, optimized electrode structure, inert matrices (if used at all) will be needed. Better solutions to chemical engineering problems are even more urgent. The best approach appears to be abandonment of the Grove cell and use of modern electrochemical knowledge in developing novel systems concepts. These may result in even greater weight and volume savings as well as simpler controls, lower parasitic power and longer life, particularly for larger power systems. Peak power and heat-load demands might best be met by special auxiliaries instead of overdesign of the basic equipment. In turn, pseudo-primary fuel cells may satisfy peak loads in conjunction with primary solar or nuclear systems.

Introduction

Among the known fuel-cell reactants, hydrogen and oxygen thus far appear to be best suited for space use. Energy densities of the reactants

in cryogenic form, including also the requisite tankage, are close to the highest that can be attained. The reactants are relatively easily stored and handled, presenting no difficult compatibility problems. Although efficiency losses at the cathode leave room for improvement of low-temperature cathodic catalysts, reactivities of both reactants are high enough to permit equipment to operate at "low" temperatures (about 100°C) and reasonable thermal efficiencies. The chemical byproduct, water, is useful for various human purposes as well as spacecraft applications, e.g., evaporative cooling and attitude control. Reactants and product thus offer a maximum of utility and a minimum of problems. No wonder, then, that H_2-O_2 cells were the first to be studied by Grove[1] in 1838, the first to be built in kilowatt size by Bacon[2] in the first half of this century, and the first to be used in NASA's Gemini[3-5] program.

In fact, regardless of temperature of operation, choice of liquid electrolyte, or type of electrode structure, all gas-fed fuel cells are still built according to Grove's prescription for maximizing the 3-phase boundary, even though several electrochemists[6-8] more recently established the fact that the locus of reaction is just below that line. I shall return to this point again later on. Suffice it to say that all hydrogen-oxygen systems contain gas plenums, porous electrodes, and electrolyte plenums in each cell.

Status

In view of the many publications and presentations[9-12] [13-17] that have described the major space systems, I shall not repeat the physical and chemical details of the Gemini ion-exchange membrane system nor those of the Apollo modified Bacon system.[18-21] The asbestos system with passive water removal has also been adequately characterized previously, as has the recirculating, free-electrolyte system,[22-25] on which we have just started to undertake some space-type modifications. It may be amusing to note en passant that the first flown system was based on Niedrach and Grubb's[26] idea of the 1950's, the second one for manned spaceflight is based on Bacon's[27] work of the 1930's and a possible third choice may be based on Mond and Langer's[28] paper of 1889; what next?

Although the performance forecast was to be made in the form of graphs, the data necessarily have to be presented in tabular form. That is because the Gemini and Apollo systems were designed about 1962 and, though modified in many details since then, were built essentially to meet these original design specifications. Allis-Chalmers' asbestos system is still being modified, apart from the fact that there are two distinct versions, one[29] for unmanned spaceflight rated at 200 watts/module (without liquid coolant), the other[30] for manned flight rated at about 1 kw/module and using the liquid coolant of the spacecraft for heat exchange. As for 1975 figures, they represent estimates, wishful or otherwise, that are not derivable by drawing curves through single points. In addition, the tables contain some "long-term" goals, for which a date has purposely not been selected.

Cell Data

Table 1 shows characteristics of single cells. The performance of fresh Apollo and asbestos cells are quite comparable. Even active cell areas are more similar than would appear from the table, since two asbestos cells are wired in parallel in the system. Similarly, the power is drawn from cell pairs in the latter device.

It remains to be seen whether the voltages and reactant consumption rates projected for 1975 can actually be obtained; perhaps a better cathodic catalyst, more severe operating conditions, or both will lead to this goal for a "low-temperature" system. Thus far, we have not found durable catalysts significantly better than platinum, palladium, or silver. Much higher cell power densities have been obtained by raising the temperature as high as 150°C, but with concommitant materials and life problems. Improved electrode structures may also aid in achieiving these goals.

As concerns degradation, more stable ion-exchange membranes are said to be under development now.[31] Stability of the Bacon cell is improved by lowering the operating temperature and compensating for the lesser activity by using catalysts. The main difficulty with the asbestos cell appears to be gradual reaction of the matrix with the electrolyte, so that asbestos must be either stablized or replaced. It is known that the same electrodes,[32] ~~suitability~~ SUITABLY wet-proofed to operate with free-flowing electrolyte, maintain their activities virtually unchanged for several hundred hours.

Opportunities for research on conventional space-type cells appear to be limited primarily to

(a) improvement of electrode structure, to increase limiting current densities by facilitating access of gas to the electrolyte;

(b) improvement of cathodic catalyst, to minimize chemical overpotential and hence inefficiency due to activation of oxygen; and

(c) replacement of membrane or matrix (if used) by a more durable structure to eliminate performance degradation due to this source. The new structure should also have high ionic conductivity and minimum thickness -- consistent with safety and acceptable electrolyte capacity -- for minimizing ohmic overpotential. There is no point in attempting to replace platinum as the anodic catalyst for space cells, though it represents a very severe handicap for commercial purposes.

System Data

Data for fuel-cell modules are given in Table 2. The power rating of these units is stated for sustained rather than for peak loads. Obviously, present systems can be derated, i.e., used at lower average power levels, if one wishes to improve efficiency and life for specific purposes. Conceivably, too, a system may eventually be improved to the point where its sustained load can be increased significantly without the penalty of lower efficiency and shorter life.

Improved Bacon modules exist today that weigh about 70% and measure about half of the values quoted. Parasitic power consumption is being lowered as more efficient auxiliary equipment becomes available and engineering design is improved. Module life is generally a fraction of cell life, apparently mainly because of lack of quality control. This is not to say that the modules are being put together carelessly. It simply

means that the factors that must be controlled, and the severity of slight variations, are often not recognized until after a number of units have been built and operated.

For example, uneven gas distribution, due to small variations in manifolding or occasional liquid plugs, may "starve" a cell. Since the gas plenum requires uniform pressure, impure residual gas may seep into that cell from its neighbors. The resulting degradation may be alleviated only briefly, if at all, by purging the stack. Since this problem has been recognized, better purge control can be achieved by means of simple inserts (that maintain individual cell pressure differentials). Such difficulties are not always easy to foresee.

An important characteristic of any device is its capability to tolerate abuse and to recover from overstress. To my knowledge, no fuel-cell system has yet been thoroughly evaluated for these properties. We have underway a first, and only partial, set of tests of this kind: A series of 8 full-size asbestos stacks is being systematically mistreated, to determine how they react to repreated start/stop operation; overloads; pressure unbalances; overheating, etc. The same procedures will eventually have to be applied to the mechanical, electrical, and electronic auxiliaries as well, if they are to be fully characterized.

In these tests, we have already learned that an asbestos stack need not be filled with helium for storage, an important simplification of procedure and equipment. Power spikes of up to 5 kw were tolerated

without catastrophic damage; duration of these spikes was limited only by the cooling capacity of the stack. Multiple starts and stops appeared to have no adverse effect. Starting at room temperature, a stack was warmed to operating condition using its own waste heat, by running it at constant voltage or constant amperage. Warm-up times ranged from 59 down to 6.5 minutes, with temperature differences through the stack varying from 20°F for the hour-long start, to 27°F for the fast start.

In contrast to the limited research opportunities in electrochemistry, engineering research on space fuel-cell systems has barely begun. Today's equipment is little more than an assembly of oversize laboratory cells with superimposed mechanical and electrical controls. We still don't know whether Grove-type cells are optimum, since no other concept has yet been engineered. The Grove cell combines two functions near and at the electrode surface, (1) dissolution of gas in electrolyte and (2) electrochemical reaction. While it would be senseless to separate these functions for a single cell or even a few cells, a separate gas saturator combined with flow-through electrodes might be feasible for large cell stacks. Will the size and complexity of such equipment, together with the power needed for pumping electrolyte through electrodes, make this scheme useless? Or what about the slurry system proposed by chemists in France [33] and Germany? [34] Some preliminary design studies [35-37] are now being made for NASA to determine the prospects of success for these approaches. Still other ideas are as yet unexplored.

The plumbing and electronics today are essentially afterthoughts -- appendages that had to be provided to make the stack operable. Perhaps

one should consider a fuel-cell plant to be a chemical reactor, with electricity as a byproduct, in ~~oder~~ ORDER to arrive at novel design concepts. Admittedly, such a reactor must operate under far from ideal conditions, particularly when compared with a reactor in a chemical factory. Nevertheless, there are many well-established ~~and novel~~ engineering concepts, for optimizing chemical plants and for incorporating automatic regulations and control, that may be directly applicable to fuel-cell plants. If the projections, shown in the last column of table 2, are ever to be attained, we must surely re-orient our engineering approach to fuel-cell systems.

Reactant Storage

Apart from electrical leads and means for removing water, a fuel-cell system also needs a supply of reactants and capability to dispose of the heat that is an inevitable byproduct. In space, both hydrogen and oxygen are stored cryogenically to avoid the weight penalty of high-pressure tankage. However, in this form the reactants are not storable for indefinite periods, because heat leaks into the storage vessels and causes some of the liquid to evaporate and boil off. The boil-off must either be used electrochemically or vented to avoid pressure build-up.

The precise ratio of weight of tankage to weight of cryogenic fluid depends on the size of the vessel, quality of insulation, ambient temperature, vessel pressure, rate of reactant usage, and state and temperature of reactant (slush, subcritical liquid, supercritical gas).

Representative figures for supercritically stored oxygen for current fuel-cell applications are 3-3.5 lb/lb tankage; and for hydrogen 0.3-0.4 lb/lb tankage. These numbers are for 20-30 lbs. of hydrogen and eight times as much oxygen. Both figures of merit might be raised by developing lighter structures for the outer shells of the Dewar vessels. A projected single tank to store both reactants would hold 4.25 lb/lb tank. Furthermore, subcritical oxygen storage might raise the above number to 4-5 lb/lb tankage. -- Theoretical storage volumes are 4.4 lb H_2/ft^3 and 71.2 lb O_2/ft^3 at atmospheric pressure and at their respective boiling points. Some 95% of the stored reactant can be made available to the fuel cells.

Heat Balance

Since the combination of hydrogen with oxygen is exothermal, heat generally must be removed from a fuel-cell power plant. During start-up or standby, however, heat may have to be added to the system. Depending on the particular system design and capabilities, starting may be a simple "bootstrapping", i.e. self-heating process, or else one needs an auxiliary heat source. This last requirement complicates the system and makes it less flexible.

Heat may be discarded by evaporative cooling. For relatively short missions, one may wish to evaporate the product water, which will extract about 1/3 of the heat evolved. The remainder can be transferred out of the system by venting hydrogen.

A transient heat load can be handled by re-injecting stored water and letting it warm up.

In general, however, most of the heat of reaction will be removed by a heat exchanger and eventually radiated to the surroundings. The size of the radiator area varies with a number of factors, among them the system's efficiency (itself a function of load); the temperature at which water leaves the fuel cell (again dependent on load as well as on the specific system); shape, position, and efficiency of the radiator; and temperature of the radiator and of the heat sink. For a complete power supply, one would also have to consider the heat load imposed by the inefficiencies of power conditioning.

For Gemini, some early published data on the radiator are: temperature, 100°F; heat flux, 30 w/ft^2; and radiator area, 25 ft^2/kw (presumably peak electrical kw). The radiator exit temperature for Apollo is 160-170°F and the effective area 24 ft^2/kw in earth orbit, 12 ft^2/kw in deep space. Under worst lunar conditions, the radiator might overheat for a few minutes. An asbestos-cell system (with water collection) is expected to have a radiator temperature of 177°F and a radiator area of 21.3 ft^2/kw in earth orbit, 13.5 ft^2/kw in deep space. The discrepancies in the design data cited may be indicative of the uncertainities of the calculations. Radiator weights are on the order of 1-2 lb/ft^2.

Other Considerations

The cost of space fuel-cell plants, exclusive of reactants, tankage, and radiator, is of the order of $100,000/kw (sustained power) today. The extraordinarily high figure reflects the fact that systems are essentially handmade and must pass rigid inspections. The same equipment,

made to less exacting standards, costs perhaps half as much. Even semi-automation should reduce the cost substantially below the $50,000 figure. Another approach to lower cost would be to improve the performance of the fuel cell so that the same size stack could produce higher power in sustained operation.

Considering the immediate space program only, the 1-kw power-plant, with 2-2.5 kw peak capacity, is adequate, especially in view of the fact that several such systems must be carried for reliability reasons. Future missions, however, may require 10 or more times that amount of power. Hence larger modules should be useful in the 70's or 80's. They should be cheaper per kw as well as lighter and more compact, assuming that performance, geometric surface area, or both these properties of electrodes can be scaled up. If the cathode remains the limiting electrode, its effective surface area is easily doubled by sandwiching one anode between two cathodes. Parastic power per stack might not decrease much in absolute value but should be a considerably smaller percentage of total stack output.

Conclusion

Finally, we must consider the future of the fuel cell in space. For long space missions, the primary source of energy can obviously not be chemical, because the weights of fuel and oxidant would become prohibitive. Nevertheless, fuel cells are likely to play a continued role in the space program.

They may be emergency and peak primary power sources in connection with both solar and nuclear power plants. They may supplement or replace secondary batteries, with the astronauts using the byproduct water before it is electrolyzed again. And they may be the sole, primary power sources for lunar surface vehicles, from which the water would be returned to an electrolyzer at the base for re-processing. On the other hand, if water should be readily available on the moon, the vehicle might use the water for evaporative cooling by day or even as a heat source at night, thus extending its mission time. Lastly, fuel cells may eventually replace primary batteries as the electric power source of rockets, although the fuel-cell system would admittedly have to become much simpler than it is now, to make it attractive for this use.

The forecasts made here are based on present-day engineering approaches. In the drive to obtain usable devices as quickly as possible, engineers have done an excellent job of building what appeared feasible. But this rush toward hardware may also have meant pushing aside ~~any~~ MANY promising, untested ideas. Now that operable systems are at hand, we should consider the more speculative approaches in an attempt to upset these predictions.

Whereas efficiencies are already quite close to the thermodynamic limits, the bulk and weight of fuel-cell systems leave much room for improvement. Similarly, longer life, greater simplicity, and more self-regulation ought to be achievable. Also, more thought must be given to optimizing the total power package, which includes not only the fuel-cell system but power conditioning as well. Perhaps a lower voltage output from the fuel cells, more electrical parralleling, and

appropriate changes in power conditioning would result in greater reliability and longer useful life, with little or no penalty in weight and volume.

Any large engineering improvements are bound to be reflected in improved physical and economic properties of fuel-cell systems, assuring their being of continued interest for space. In addition, such changes are bound to make them more attractive commercially, thus hastening their acceptance in terrestrial applications.

TABLE 1

CHARACTERISTICS OF INDIVIDUAL CELLS

				Goals	
	Gemini	Apollo	Allis-Chalmers	1975	Long Term
Current density, a/ft^2 ($\doteq ma/cm^2$)	15	92	100	200	400
Initial voltage, volt	0.8	0.97	0.95	1.0	1.1
Power density, w/ft^2 ($\doteq mw/cm^2$)	12	89	95	200	440
Active cell area, ft^2 ($\doteq 0.1\ m^2$)	0.375	0.4	0.2	-	-
Cell power, watts	4.5	35.6	19	-	-
Reactant consumption, lb/kw ($\doteq$0.45 kg/kw)	0.9	0.8	0.8	0.76	0.7
Degradation rate, mv/1000 hrs.	50-100	60	40	4	<4
Principal degradation mode	membrane decomposes	cathode corrodes	asbestos reacts		

NOTE: Data are for sustained, not peak, power.

TABLE 2

CHARACTERISTICS OF FUEL-CELL MODULES

				Goals	
	Gemini	Apollo	Allis-Chalmers	1975	Long Term
Module size, kw (sustained power)	0.5	1	1	2.5-5	5-10
Module weight, lb/kw (≐ 0.45 kg/kw)	140[a]	268	165	<70	<30
Module volume, ft^3/kw (≐ 28.3 l/kw)	6	10.7	5.7	-	-
Stack volume, ft^3/kw (≐ 28.3 l/kw)		4.75	2	<0.9	<0.35
Parasitic power, w/module	0[a]	75[b]	50[c]	< 50	< 50
Life under load, hrs.	400-800	400-1500	1000-2000	10,000	10,000+
Storage at room temperature and below	good[d]	good[e]	good	wide temperature range	
Heating time, room to operating temp., min.	0	60	15-30	<15	<15
Auxiliary heater, kw	0	3	0	0	0
Recovery from abuse	poor	poor	good	broad tolerance	

NOTE: a. Integration of the fuel-cell and environmental control systems complicate these estimates; a separate power system would have weighed more and required parasitic power.

b. This is alternating current and does not reflect losses in power conditioning.

c. This is the total power drawn from the d.c. supply.

d. This is before activation; once activated, the stored system degrades by 0.2-0.7 volt/1000 hrs.

e. System stores well even up to 200°F (94°C).